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PATENT SPECIFICATION

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(54) INHIBITION OF PERSPIRATION

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to the inhibition of perspiration. More especially the invention relates to methods of inhibiting perspiration, packages consisting of the combination of an antiperspirant composition and an applicator for applying the antiperspirant composition to the skin, and to antiperspirant compositions suitable for use in such methods and packages. Other aspects of the invention relate to solid antiperspirant compounds and aqueous solutions suitable for use in such compositions as well as to processes for making such compounds and aqueous solutions.

For inhibiting perspiration, the application to the skin of many different antiperspirant active compounds has been described in the literature. However, those compounds most widely used in commercial products at the present time are basic aluminium halides, especially aluminium chlorhydrate, which has an Al/Cl molar ratio of about 2. These active compounds are applied to the skin from a variety of applicator types including aerosol sprays, pump sprays, squeeze packs, roll-ons and stick applicators. Thus aluminium chlorhydrate, for example, is employed as the active ingredient of various liquid, cream, stick or dry powder antiperspirant compositions. However, in spite of the popularity of aluminium chlorhydrate the presently available products are capable of producing only limited reduction in perspiration.

It is an object of the invention to provide an improvement in the reduction of perspiration.

The present invention is based on our discovery that in the employment of certain basic aluminium chloride, bromide, iodide and nitrate compounds, an improvement in antiperspirant efficacy is obtained through the use of those forms which in aqueous solution contain polymeric species having a size greater than 100 Angstroms in which species there is contained from 2 to 80% by weight of the total aluminium.

Since in aqueous solutions of the basic aluminium compounds the halide or nitrate is in ionic form the polymeric species present are hydroxyaluminium species.

In one aspect therefore the invention relates to a method of inhibiting the exudation of perspiration by applying to the skin a polymeric antiperspirant compound which is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound forms in water an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

The invention also relates to a package consisting of the combination of an antiperspirant composition comprising an antiperspirant active compound and an applicator for applying the antiperspirant composition to the skin, wherein the antiperspirant active compound is a basic aluminium chloride, bromide, iodide or

nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound forms in water an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

Preferably the species having a size greater than 100 Angstroms contain from 5 to 60% by weight of the total aluminium. The solutions of polymeric basic aluminium compounds referred to herein are meant to include not only true solutions but also colloidal solutions or dispersions. Such solutions may contain large colloidal polymeric species the upper limit for the size of which is not critical, it being required, however, that they can be dissolved or stably dispersed in water to form a colloidal solution. Usually, however, there will not be any substantial amount of polymeric species exceeding 1,000 Angstroms in effective diameter, although the aqueous solutions may be hazy or cloudy in appearance.

The package according to to the invention may be one in which the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises a suspension of said antiperspirant active compound in particulate form in a liquid carrier which may be in admixture with a propellant. Furthermore, the package may be one wherein the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of said antiperspirant active compound. In this case the aqueous solution may be discharged by a propellant gas or by a finger-operated pump mechanism or by containing the composition within a container of pliable material whereby by squeezing the container the composition is expelled through the spray valve. Another form of package is one in which the applicator is a roll-on applicator and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of the said antiperspirant active compound. Furthermore, the package may be one wherein the applicator is an applicator for dispensing a powdered material and the antiperspirant composition is a powdered composition including said antiperspirant active compound in powder form. The applicator may also be a stick applicator for holding an antiperspirant composition in the form of a stick or it may be tissue or cloth which is impregnated with the antiperspirant active material.

In accordance with another aspect of the invention there is provided an antiperspirant composition comprising an aqueous solution of an antiperspirant active compound in combination with an adjunct which is a perfume, thickener, alcohol or propellant, wherein said compound is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, said aqueous solution containing polymeric species having a size greater than 100 Angstroms within which species there is present from 2 to 80% by weight of the total aluminium. The antiperspirant composition may be in the form of a lotion comprising an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight and 0.1 to 5% by weight of a thickening agent. Suitable thickening agents for antiperspirant lotions are well known to those skilled in the art, and include for example, magnesium aluminium silicates. Thickening may also be effected by emulsifying an oil in the composition. Furthermore, the composition may comprise an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight and from 0.1 to 1% by weight of perfume.

The composition may comprise an aqueous alcoholic solution of the basic aluminium compound containing from 1 to 60% by weight of an alcohol. these aqueous alcoholic compositions preferably contain ethanol or isopropanol as the alcohol which are preferably present in an amount of from 1% to 30% by weight of the composition. Antiperspirant compositions comprising an aqueous solution of the active compound may contain from 1 to 80% by weight of a propellant.

The antiperspirant composition may also comprise in combination a powdered antiperspirant active compound and a powdered inert solid diluent or organic liquid carrier, wherein said compound is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, which compound forms when dissolved in water and aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium. The composition may be in the form of a powder aerosol composition comprising a suspension of the basic aluminium compound in particulate form in a liquid carrier, said composition also comprising a propellant. In particular the

composition may be in the form of a powder aerosol composition comprising

A. from 1% to 12% by weight of said basic aluminium compound in powder form;
B. from 0.1% to 5% by weight of a suspending agent;
C. from 1% to 15% by weight of a carrier liquid; and
D. from 70% to 96% by weght of a propellant.

The carrier liquid may for example be a non-volatile non-hygroscopic liquid as suggested in US Patent No. 3,968,203. Especially useful are carrier liquids which have emollient properties and a number of these are referred to in British Patent Specification No. 1,393,860. Especially preferred are fatty acid esters such as isopropyl myristate and those esters referred to in British Patent Specification No. 1,353,914 such as dibutyl phthalate and diisopropyl adipate.

Various other carrier liquids for powder suspension aerosols are suggested in US Patent Specifications Nos. 3,833,721, 3,833,720, 3,920,807, 3,949,066 and 3,974,270 and in British Patent Specifications Nos. 1,341,748, 1,300,260, 1,369,872 and 1,411,547. Volatile carrier liquids may also be used such as ethanol as described in South African Patent Specification No. 75/3576, and volatile silicones.

The ratio of total solids in the compositions to the carrier liquid may vary over a wide range, for example from 0.01 to 3 parts of the powder per part by weight of the carrier liquid.

The propellant can be a liquefied hydrocarbon, halogenated hydrocarbon or a mixture thereof. Examples of materials that are suitable for use as propellants are given in the above-mentioned patents and include trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, thrichlorotrifluoroethane, propane, butane, 1,1-difluoroethane, 1,1-difluoro-1-chloroethane, dichloromonofluoromethane, methylene chloride, isopentane and isobutane, used singly or admixed. Trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, and isobutane, used singly or admixed, are preferred.

Examples of materials that are suitable for use as permanent gas propellants are nitrogen, carbon dioxide and nitrous oxide.

It is common practice to include in aerosol powder spray compositions a material to assist in the suspending of the powder in the liquid vehicle. The materials prevent compacting of the powder and they may also act as thickening or gelling agents for the liquid vehicle. Especially preferred are hydrophobic clays and colloidal silicas. Hydrophobic clays are available under the trade mark "Bentone", e.g. Bentone 34 or Bentone 38, and their use as suspending agents are described in a number of patent specifications including US Patent Specification No. 3,773,683. Suitable colloidal silicas include Aerosil 200 and Cab-O-Sil M-5 as well as other grades (the words "Aerosil" and "Cab-O-Sil" are trade marks).

The antiperspirant composition may, however, simply comprise from 5 to 40% by weight of said basic aluminium compound in powder form, the remainder consisting essentially of an inert powder material, such as talc or starch, for example.

The basic aluminium compound may have the empirical formula

$$Al_2(OH)_{6-a}\,X_a$$

where X is Cl, Br, I or No_3
a is from 0.4 to 1.5
the formula in the case of the compound in solid form containing 0.5 to 8 molecules of water of hydration. Preferably the basic aluminium compound has an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 4 to 1.6:1, more particularly 2.5 to 1.6:1.

The invention also relates to a solid antiperspirant compound comprising a hydrated basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound when dissolved in water forms an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium. The solid antiperspirant compound may have the empirical formula

$$Al_2(OH)_{6-a}\,X_a\,nH_2O$$

where X is Cl, Br, I or NO_3,

a is from 0.3 to 1.5

n is from 0.5 to 8.

In particular a may be from 0.5 to 1.5, preferably from 0.8 to 1.25. The solid compound preferably contains 0.5 to 4 molecules of water of hydration. A form of said solid compound particularly suitable for use in aerosol powder spray compositions is one comprising particles having a size less than 100 microns, preferably less than 44 microns.

In a further aspect, the invention relates to an aqueous solution of an antiperspirant compound in a concentration of 7 to 15% by weight, said compound being a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3

a is from 0.3 to 1.5, preferably from 0.4 to 1.25

said solution containing polymeric species having a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium present in said compound, said solution being free of boehmite as determined by X-ray diffraction on the material dried at 50°C under vacuum.

There is also provided by the present invention an aqueous solution of an antiperspirant compound, wherein said compound is a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3

a is from 0.3 to 0.9 or from 1.1 to 1.5

said solution containing polymeric species having a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

The invention also relates to an aqueous solution of a basic aluminium bromide, iodide or nitrate having an aluminium to bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, which solution contains polymeric species of the basic aluminium compound of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium. The solution may comprise the antiperspirant compound in a concentration of from 1 to 60% by weight, and said compound may be a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Br, I or NO_3

a is from 0.3 to 1.5, preferably from 0.4 to 1.25.

For the above compounds and solutions, there is preferably contained within the polymeric species having a size greater than 100 Angstroms from 5 to 60% by weight of the total aluminium.

The above-described special forms of basic aluminium compounds which in aqueous solution contain polymeric species having a size greater than 100 Angstroms within which from 2 to 80% by weight of the total aluminium is contained, may be prepared by heating aqueous solutions of the basic aluminium compounds at elevated temperature, as more particularly described herein. The production of the desired species depends on the appropriate choice of the reaction conditions which are inter-related. It is preferred to use temperatures of from 80°C to 140°C. The period of heating may be shorter as higher temperatures are used, ranging for example from 0.5 hour to 30 days. Of importance is the concentration of the basic aluminium compound. At the above temperatures, substantially no production of the higher polymeric species of the basic aluminium compound has been observed with solutions having a concentration above about 40% by weight. At these temperatures the concentration of the solution should be no more than about 35% by weight.

The conditions of heat treatment described above have been found to give rise to the improved basic aluminium compound in amorphous form, and in particular the formation of boehmite, as determined by X-ray diffraction, has not been

observed. The production of a substantial amount of boehmite or other crystalline forms of alumina would be considered to be disadvantageous.

According to the invention a preferred process for making an aqueous solution of an antiperspirant compound comprises heating an aqueous solution of a compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.3/to 1.5
said solution having a concentration of from 7 to 35% by weight, at a temperature of from 80°C to 140°C for a time sufficient to give rise in said solution to polymeric species having a size above 100 Angstroms in such amount that from 2 to 80% by weight of the total aluminium is contained within such species.

A further embodiment of the production of an improved solution of an antiperspirant compound comprises heating an aqueous solution of a compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Br, I or NO_3
a is from 0.3/to 1.5
the concentration of such solution and its temperature and time of heating being such that there is produced in the solution polymeric species having a size above 100 Angstroms, said species being produced in such amount that from 2 to 80% by weight of the total aluminium is contained within such species.

The aqueous solution of the more active antiperspirant compound comprising the higher polymeric species as defined, may, if desired, be evaporated to concentrate the solution or it may be dried to give the compound in the form of a solid hydrate. As with untreated aluminium chlorhydrate, for example, drying conditions which lead to both the loss of water of condensation, between the hydroxy groups of the compound, and hydrochloric acid should be avoided as these may lead to irreversible degradation of the treated basic aluminium compound. Any suitable method of drying may be used, spray drying being a particularly useful method. The spray drying method described in US Patent No. 3,887,692 may be employed. The solid material may be ground or milled as required.

Accordingly a preferred method of making an improved solid hydrated antiperspirant active compound comprises spray drying an aqueous solution of a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, said solution containing polymeric species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

The above processes are preferably conducted in such manner that within said species there is contained from 5 to 60% by weight of the total aluminium.

The test methods for testing antiperspirant efficacy of various antiperspirant compositions referred to in the Examples given herein will now be described.

TEST METHOD FOR ASSESSMENT OF EFFICACY OF ANTIPERSPIRANTS

In the Examples given herein five test methods are referred to for the assessment of various antiperspirant active agents referred to therein. Details of the test procedures are described below.

Test Methods I to IV for the assessment of antiperspirant efficacy depend on subjecting human volunteers to thermal stress and gravimetric determination of axillar sweat.

Test Method I

Subjects

A panel of up to 18 women use no antiperspirant for the 14 days before the test or during the 16 day interval between the two halves of the test.

Hot room

Temperature 37°C ± 1°C, relative humidity approximately 35%.

Products

Two to four products are tested, one of which is designated as the control. Each subject receives a different treatment on each axilla and as far as possible equal numbers of left and right axillae receive each treatment.

Product Application

A two-second spray is administered.

Sweat Collection

Absorbent cotton pads are used to collect the sweat. On entering the hot room each subject has a pair of pads placed in her axillae. After 40 m,inutes these are removed and rejected. Sweat is then collected for two consecutive periods of 20 minutes, fresh tared pads being used for each collection, and sweat weight determined.

Test Design

On the first day of the test the subjects receive treatment with the test products but do not undergo a hot room sitting. On each of the next 4 days they undergo hot room sittings, with treatment immediately before each sitting and after showering. The final treatment is omitted on the fifth day. After an interval of 16 days the subjects return and the whole procedure is repeated, with the two products received by each subject applied to the opposite axillae.

Analysis of Data

The statistical treatment includes an analysis of variance which allows for subject, side and product effects. The efficacy is calculated from the geometric mean weight of sweat collected from the axillae treated with each product.

$$\%\ \text{reduction} = 100\frac{(C - T)}{C}$$

where C is the geometric mean sweat weight from the axillae treated with the control product and T is the geometric means sweat weight from the axillae treated with the test product. The % reduction is usually calculated for each day separately and for the entire test.

Significance is calculated by applying Duncan's Multiple Range Test to the logarithmically transformed weights.

Test Method II

Subjects

A panel of up to 54 women who use no antiperspirant for the 14 days before the test.

Products

Two aerosol poeder spray products of which one is designated the control. The panel is divided into two equal groups. One group receives the test treatment on the left axilla and the control treatment on the right, while the second group receives them the other way round.

Test Design

Subjects attent daily for 3 consecutive days. They receive one treatment with the products each day. On the third day the treatment is immediately followed by a hot room sitting and sweat collection.

Analysis of Data

As for Test method I except that significance is calculated by applying Student's t-test to the logarithmically transformed weights.

The products used in Test Methods I and II had the composition indicated below.

Ingredient	Test Product I (%)	Test Product II (%)
Treated or untreated aluminium chlorhydrate	3.50	4.50
Isopropyl myristate	3.25	6.00
Pyrogenic silica (Aerosil 200)	0.10	0.45
Perfume	0.44	0.44
Propellant[1]	to 100.00	to 100.0

[1] CCl_3F:CCl_2F_2—65:35 by weight (Product I)
50:50 by weight (Product II)

Test Method III

As Test Method II with the following differences:

Test Product
10% solution of treated aluminium chlorhydrate (unless stated otherwise) in water.

Control Product
10% solution of untreated aluminium chlorhydrate (unless stated otherwise in water.

Method of Application
Approximately 0.5 g of solution was applied to each axilla with a cotton swab.

Test Method IV

As Test Method III with the following differences:

Method of Application
Approximately 0.5 g of solution was aplied to each axilla with a pump-spray applicator.

Test Method V

This method is the Forearm Starch Iodine Patch Test which was conducted as follows (after Wada & Tokayaki in J. Exp. Med. *49* 284 (1948)).

A panel of volunteer test subjects was recruited and each panellist had a number of test solutions applied to separate sites on the volar aspect of the forearm. The solutions (12 drops) were applied under semi-occlusive patches and left for 6 hours. The treatment region of the forearm was then painted with several coats of a 1% solution of iodine in alcohol. After evaporation of the alcohol, the painted area was covered with a 50% suspension of starch powder in oil. The subject was then placed in a heated room (40 ± 2°C) until sweating commenced. The effectiveness of the various treatments was then assessed on the basis of the number and size of blue spots arising from the interaction of starch, iodine and sweat.

Determination of percentage aluminium in polymeric species having a size greater than 100 Angstroms

All heat-treated basic aluminium compounds described herein were defined by molecular sieve chromatography. For this purpose there was used a 1.2 m × 6.0 mm column packed with spherical porous silica beads of particle size 75—125 microns, and of surface area 350—500 m²/g, and having a maximum pore size of 100 Å. The silica employed, available commercially as Porasil AX, had been deactivated to eliminate adsorption in molecular size separations (the word "Porasil" is a trade mark). The use of Porasil silica beads as a column packing in

chromatography is referred to in "Gel Permeation Chromatography" by K. H. Altgelt and L. Segal, 1971, pages 16 to 18. The silica was conditioned before use by passage of a single large sample (e.g. 0.5 ml of a 2% $^w/_w$ solution) of a heat-treated aluminium chlorhydrate. Samples to be tested were made up in deionized water to approximately 0.2 M aluminium and thoroughly dispersed by treatment (4 minutes) with a sonic probe. About 0.1 ml samples of approximately 0.2 M aluminium solutions were applied to the column by a sample loop system and eluted with 10^{-2} M aqueous hydrochloric acid solution using a peristaltic pump. A differential refractive index monitor linked to a pen recorder was used to detect fractions as they were eluted. These fractions were collected and analysed for aluminium by atomic absorption. Complete elution of all aluminium applied in each sample was checked by direct analysis of another sample of the same volume. The percentage of the total aluminium which appeared in the fraction eluted at the void volume of the column was considered as that deriving from polymeric material of a size greater than 100 Å in effective diameter. None of this polymeric material was found in any untreated aluminium chlorhydrate solutions.

Determination of water content of powdered materials

The water content of powdered materials was estimated by thermogravimetric analysis (TGA). On heating to 1,000°C, aluminium chlorhydrate undergoes the following reaction:

$$Al_2(OH)_5Cl(H_2O)_x \rightarrow Al_2O_3 + HCl\uparrow + (x + 2)H_2O\uparrow$$

From a knowledge of Al/Cl ratio of the material (and hence the empirical weight of the anhydrous $Al_2(OH)_{6-a}Cl_a$) it is possible to calculate the number of moles of water (x) associated with each anhydrous unit from an accurate determination of the weight loss on heating a known weight of sample to 1,000°C. The following equation shows the method of calculation:

$$x = \frac{\left(\dfrac{\text{Weight of solid before heating}}{\text{Weight of solid after heating}} \times 102\right) - \begin{array}{l}\text{Empirical weight}\\ \text{of anhydrous}\\ [Al_2(OH)_{6-a}Cl_a]\end{array}}{18}$$

The percentage of water is given by

$$\frac{1{,}800x}{\text{Empirical weight of anhydrous } Al_2(OH)_{6-a}Cl_a + 18x}$$

The following Examples illustrate the invention.

Example 1.

Aluminium chlorhydrate powder having an Al/Cl molar ratio of 2.04 and a water content of 18.5 was dissolved in deionized water so as to give a 10% $^w/_w$ solution. This solution was heated in 1 litre screw-cap glass bottles to 96°C over 9 hours and then held at this temperature for a further 39 hours. The resulting solution was cooled to room temperature and found to contain 27.3% of the total aluminium as polymers exceeding 100 Å in effective diameter. The treated solution was spray dried in a co-current spray drier using inlet and outlet temperatures of 250°C and 95°C, respectively. The resulting powder had an Al/Cl molar ratio of 2.10 and a water content of 14.2%. The powder was sieved to obtain a fraction between 30 and 50 microns.

The spray dried powder was tested for antiperspirant efficacy in two tests using Test Method I.

Test No. 1

This test involved 17 subjects.

Test Products

Test Product I made with the treated aluminium chlorhydrate. Two Test Products I made with untreated aluminium chlorhydrate drawn from two different production batches.

Control Product

An alcohol-based deodorant.

Results

Percent reductions for the products against the control are shown in Table I. "Day 2" refers to the combined results for the second days of each of the 2 weeks, and so on through the table. The table gives the mean of the results for the two products containing untreated aluminium chlorhydrate.

TABLE I.

Test Product	Day 2	Day 3	Day 4	Day 5	Overall
With untreated aluminium chlorhydrate	7	15	22	22	17
With treated aluminium chlorhydrate	32	42	47	56	45

The differences between the antiperspirants with treated and untreated aluminium chlorhydrate were significant at the 1% level.

Test No. 2

This was a repetition of Test No. 1 using the same products on 14 different subjects.

Results

Percent reductions for the products against the control are shown in Table II where the column headings have the same meanings as before.

TABLE II.

Test Product	Day 2	Day 3	Day 4	Day 5	Overall
With untreated aluminium chlorhydrate	22	16	29	28	24
With treated aluminium chlorhydrate	34	37	44	44	40

The differences between the antiperspirants with treated and untreated aluminium chlorhydrate were again significant at the 1% level.

Example 2.

A batch of Reheis aluminium chlorhydrate Microdry, Ultrafine grade having an Al/Cl molar ratio of 2.04 and a water content of 18.5% was dissolved in deionized water to give a 10% w/w solution (the word "Reheis" is a trade mark). This solution was heated in 1 litre screw-cap glass bottles to 97—100°C over 10 hours and then held at this temperature for a further 38 hours. The resulting solution was cooled to room temperature and found to contain 23.9% of the total aluminium as polymers exceeding 100 Å in effective diameter. The solution was tested for antiperspirancy according to Test Method III using a test panel of 46 subjects. The test solution produced a reduction of 22% in the sweat collected compared with the control (10% solution of untreated aluminium chlorhydrate solution), which was statistically significant at the 0.1% level.

The treated solution was then sprayed dried and the powder sieved as described in Example 1 to give a material with an Al/Cl molar ratio of 2.14 and a water content of 14.3%. The powder was tested according to Test Method II (with 43 panellists) using a suspension-type aerosol antiperspirant of formula according to Test Product I. The product containing the treated aluminium chlorhydrate gave a 25% reduction in sweat compared with the control product containing the untreated aluminium chlorhydrate which was significant at the 0.1% level.

Example 3.

5.0 kg of Reheis aluminium chlorhydrate having an Al/Cl molar ratio of 2.15 and a water content of 16.1% was dissolved in 45 litres of deionized water at 50—60°C in a 50 litre stainless steel reactor internally spray-coated with polytetrafluoroethylene and equipped with a propeller stirrer and partial steam jacket. The solution was stirred and heated to 100°C in the closed reactor over 10 minutes, then held at this temperature with stirring for 48 hours. After this time the solution was cooled to ambient temperature and homogenised to disperse any gel that may have been formed. The solution contained 43.3% of the total aluminium as polymers greater than 100 Å in effective diameter. When tested for antiperspirancy according to Test method III with a panel of 19 subjects and using as control the 10% solution of treated aluminium chlorhydrate of Example 2, the test solution produced a reduction of 10% in the sweat collected, the difference being statistically significant at the 10% level.

Example 4.

5.0 kg of aluminium chlorhydrate (sold as Reheis aluminium chlorhydrate Microdry, Ultrafine grade) having an Al/Cl molar ratio of 2.15 and a water content of 16.1% was dissolved in 45 litres of deionized water at 50—60°C in the reactor described in Example 3. The solution was stirred and heated to 120°C in the closed reactor over 15 minutes, and then held at this temperature with stirring for 6 hours. After this period, the solution was cooled to 90°C over 15 minutes, then discharged into a holding vessel and allowed to cool to ambient temperature. Before further treatment, the solution was passed through a homogeniser. This solution contained 40.8% of the total aluminium as polymers exceeding 100 Å in effective diameter. When tested for antiperspirancy according to Test Method III with a test panel of 42 subjects and using as control the 10% solution of the treated aluminium chlorhydrate of Example 3, the solution produced a reduction of 1% in the sweat collected. The difference was not statistically significant at the 5% level.

A portion of the treated solution was spray dried by the method described in Example 1. The resulting powder had an Al/Cl ratio of 2.23 and a water content of 11.2%. The powder was seived to obtain a fraction between 30 and 50 microns which was incorporated into a suspension-type aerosol antiperspirant (Test Product II formula) and compared according to Test Method II (using a panel of 51 subjects) with a once commercially available highly effective powder spray product based on a zirconium/aluminium complex as control and found to give a reduction of 7% in the sweat collected. This was not statistically significant at the 5% level.

When a sample of the spray dried powder was heated for 24 hours at 120°C the dried product obtained had the empirical formula $Al_2(OH)_{5.31}Cl_{0.69}$. The solution obtained on dissolving this anhydrous powder in water was shown to contain 45.4% by weight of the total aluminium in polymers having an effective diameter of more than 100 Å.

Example 5.

10 kg of a 50% $^{w}/_{w}$ solution of aluminium chlorhydrate (available commercially under the trade mark "Chlorhydrol") which had an Al/Cl molar ratio of 2.09, was added to 40 litres of deionized water and the resulting solution was stirred and heated at 120°C for 6 hours in the closed reactor as described in Example 3. The treated solution contained 32.9% of the total aluminium as polymers exceeding 100 Å in effective diameter and when compared by Test Method III on a panel of 45 subjects with the 10% solution of treated aluminium chlorhydrate of Example 4 as control gave a 2% increase in the sweat collected but this was not statistically significant at the 5% level.

A portion of the treated solution was concentrated under vacuum in a rotary evaporator at 40°C to give a solution which was 1.62 molar in aluminium equivalent to 17.1% treated aluminium chlorhydrate.

A further portion of the solution was spray dried by the procedure described in

Example 1 to give a powder which had an Al/Cl molar ratio of 2.05 and a water content of 12.7%. A sample of this powder was redissolved in deionized water and was shown to contain 32.4% of the total aluminium as polymers of a size exceeding 100 Å. The powder was sieved to give a 30—50 micron fraction which was formulated into a suspension-type aerosol antiperspirant (Test Product II). this was compared using Test Method II (involving 48 panellists) with the same powder spray control as used in Example 4 and it gave a 14% reduction in sweat collected which was statistically significant at the 5% level.

Example 6.

A solution of aluminium chlorhydrate was prepared as described in Example 3 and was stirred and heated to 120°C in the closed reactor over 15 minutes. Stirring and heating at this temperature was continued and after 1 hour, 6 hours and 25 hours samples of approximately 2 kg of the solution were withdrawn from the reactor, cooled rapidly to room temperature and homogenised. These solutions contained 19.4%, 45.1% and 78.4%, respectively, of their total aluminium as polymers exceeding 100 Å in effective diameter. The results of antiperspirancy tests on these materials by Test Method IV are included in Table III.

Example 7.

Reheis aluminium chlorhydrate, Microdry, Ultrafine grade having an Al/Cl molar ratio of 1.91 and a water content of 18.8% was dissolved in deionized water to give a 10% w/w solution. This solution was placed in 25 ml Pyrex screw-cap tubes equipped with polytetrafluoroethylene washers and heated to 115°C in an oil bath for 2 hours (the word "Pyrex" is a trade mark). The solutions were cooled to ambient temperature and found to contain 5.3% of the total aluminium as polymers greater than 100 Å in effective diameter. The result of antiperspirancy testing of this solution, by Test Method IV, is shown in Table III.

TABLE III

Test Solution	% of Total Al as Polymers Greater Than 100 Å	Control Solution	% Difference[3]	Significance Level (%)	No. of Subjects	Estimated % Reduction if Tested Against Water
10% untreated ACH[1]	0	water	-20	5	24	20
10% treated ACH	5.3	10% ACH	- 8	20	24	26
10% treated ACH	19.4	10% ACH	-21	5	22	37
10% treated ACH	45.1	10% ACH	-30	5	24	44
10% treated ACH	78.4	10% treated ACH[2]	+24	5	24	31

[1] ACH = aluminium chlorhydrate.

[2] Product of Example 6 containing 45.1% aluminium as polymers greater than 100 Å.

[3] A minus sign shows that the test solution gave a reduction in sweating compared to the control.

Example 8.

70 kg of a Reheis aluminium chlorhydrate having an Al/Cl molar ratio of 1.91 and a water content of 18.8% was dissolved in 630 kg of deionized water at 45°C and stirred and heated to 120°C in a stainless steel reactor over 3.75 hours. Stirring and heating at this temperature was maintained for a further 5.5 hours before cooling rapidly to 70°C and more slowly to ambient temperature. The resulting solution contained 41.0% of the total aluminium as polymers exceeding 100 Å in effective diameter.

Example 9.

140 kg of Reheis "Chlorhydrol" solution having an Al/Cl ratio of 2.09 was diluted with 560 litres of deionized water at 45°C and treated in a similar manner in the reactor as described for the solution in Example 8. The resulting solution was found to contain 30.6% of the total aluminium as polymers greater than 100 Å in effective diameter.

Example 10.

30%, 20%, 15%, 5% and 2% w/w solutions of a Reheis aluminium chlorhydrate having an Al/Cl ratio of 1.91 and a water content of 18.8% were prepared and heated to 120°C in 25 ml Pyrex glass screw-cap tubes, equipped with polytetrafluoroethylene washers, in a fan oven for 6 hours. The resulting solutions contained 0%, 6.3%, 20.8%, 31.1% and 21.6% respectively, of the total aluminium as polymers exceeding 100 Å in effective diameter.

Example 11.

A more acidic aluminium chlorhydrate was prepared by mixing together 19.0 g of an aluminium chlorhydrate, having an Al/Cl molar ratio of 1.91 and a water content of 18.8%, 2.25 g of aluminium chloride hexahydrate and sufficient deionized water to give 1 kg of solution. Some of this solution was placed in 25 ml Pyrex screw-cap tubes equipped with polytetrafluoroethylene washers and heated to 120°C for 24.5 hours in a fan oven. The solutions were cooled to ambient temperature and found to have an Al/Cl ratio of 1.6. 40.5% of the total aluminium in this solution was found in polymers greater than 100 Å in effective diameter.

Example 12.

A more basic aluminium chlorhydrate solution was prepared by heating a solution of 36.3 g of aluminium chloride hexahydrate in 150 g of deionized water in the presence of 145 g of 0.5 mm thick aluminium metal sheet, subdivided to approximately 6 mm squares, at 90°C for 31 hours. After cooling to room temperature the solution was decanted from the excess aluminium and found to have an Al/Cl molar ratio of 2.5 and 0% of the total aluminium as polymeric species exceeding 100 Å in effective diameter. This solution was diluted to an aluminium concentration of 0.95 M and a portion of the diluted solution was heated at 120°C for 8 hours in 25 ml Pyrex glass screw-cap tubes, fitted with polytetrafluoroethylene washers, in a fan oven. The cooled solution contained 37.6% of the total aluminium as polymeric species exceeding 100 Å in effective diameter and when compared by Test Method IV, on a panel of 20 subjects, with the non-heat-treated diluted solution as control, gave a 36% decrease in the sweat collected which was significant at the 0.1% level.

Example 13.

A 10% w/w solution of a basic aluminium bromide having an Al/Br molar ratio of 2 and a water content of about 22% was prepared and heated to 100°C in a 1 litre screw-cap glass bottle for 62 hours in a fan oven. The resulting solution was immediately cooled to room temperature and found to contain 46.4% of the total aluminium as polymers exceeding 100 Å in effective diameter. When tested for antiperspirancy using Test Method V this solution was found to be appreciably more effective than an untreated solution of the basic aluminium bromide at the same concentration.

Example 14.

A basic aluminium nitrate was prepared by dissolving 37.4 g of aluminium nitrate nonahydrate in deionized water to give 200 g of solution. The solution was heated to 90°C under a reflux condenser and 13.45 g of aluminium powder was added in small portions over a period of 5 hours. Heating was then continued with stirring for a further 24 hours. After this period, the solution was cooled to room temperature and filtered to remove excess aluminium and was found to have an Al/nitrate molar ratio of 2.9. 41.9% of the total aluminium in this solution was found in species which were greater than 100 Å in effective diameter. Some of this solution was diluted to be 0.1 M in aluminium and tested for antiperspirancy using Test Method V and was found to be equivalent in efficacy to the solution prepared in Example 2 at the same aluminium concentration.

Comparative Example.

A 50% w/w solution of a Reheis aluminium chlorhydrate having an Al/Cl molar ratio of 1.91 and a water content of 18.8% was prepared and heated to 120°C in 25 ml Pyrex glass screw-cap tubes, equipped with polytetrafluoroethylene washers, in a fan oven for 24 hours. The resulting solution contained 0% of the aluminium in polymers exceeding 100 Å in effective diameter. When tested for antiperspirancy as a 10% w/w solution according to Test Method IV, on a panel of 46 subjects, this solution gave 2% increase in the sweat collected compared to an untreated solution

of aluminium chlorhydrate of the same concentration. This result was not statistically significant at the 5% level.

The following Examples 15 to 25 are of various formulations which may be made from the treated basic aluminium compounds described in the preceding Examples 1 to 14. Percentages are by weight. For the sake of simplicity the treated aluminium antiperspirant in powder and solution form are referred to herein as "treated powder" and "treated solution", respectively.

Examples 15 to 20 are of powder aerosol spray compositions of the suspension type which are employed with an aerosol applicator.

Example 15.

	%
Treated powder	3.50
Isopropyl myristate	3.50
Aerosil 200 (pyrogenic silica)	0.10
Perfume	0.44
Propellant[1]	q.s. 100.00

[1] CCl_3F:CCl_2F_2 65:35 by weight

Example 16.

	%
Treated powder	4.50
Isopropyl myristate	6.00
Aerosil 200 (pyrogenic silica)	0.45
Perfume	0.44
Propellant[1]	q.s. 100.00

[1] Propellant CCl_3F:CCl_2F_2 50:50 by weight

Example 17.

	%
Treated powder	3.50
Isopropyl myristate	8.00
Bentone 38 (hydrophobic clay)	0.60
Ethyl alcohol (95%)	0.27
Perfume	0.40
Propellant[1]	q.s. 100.00

[1] Propellant CCl_3F:CCl_2F_2:$CClF_2$—$CClF_2$:n-butane 20:10:50:20 by weight

Example 18.

	%
Treated powder	3.50
Dibutyl phthalate	8.00
Stearoyl monoethanolamide	0.60
Perfume	0.40
Propellant[1]	q.s. 100.00

[1] Propellant CCl_3F:CCl_2F_2:butane 40:30:30 by weight

Example 19.

	%
Treated powder	4.00
Isopropyl myristate	6.00
Methylene chloride	25.00
1:1:1 trichloroethane	5.00
Aerosil 200 (pyrogenic silica)	0.45
Butane 40[1]	59.55

[1] Isobutane-propane mixture having a vapour pressure of 40 psig at 70°F.

Example 20.

	%
Treated powder	4.00
Bentone 38 (hydrophobic clay)	0.40
Isopropyl myristate	6.00
Perfume	0.50
Propellant 142b (CH_3CClF_2)	89.10

Example 21.

The following is an example of an antiperspirant lotion suitable for use with a roll-on applicator.

	%
Treated powder	5.00
Urea	5.00
Ethanol	50.00
Water	35.00
Tween 80 (polyoxyethylene sorbitan monooleate)	5.00

The word "Tween" is a trade mark.

Example 22.

The following is an example of an antiperspirant lotion suitable for use with a roll-on applicator.

	%
Treated solution (12.5%)	80.00
Glyceryl monostearate (Arlacel 165)	10.00
Distilled water	10.00

The word "Arlacel" is a trade mark.

Example 23.

The following is an example of an antiperspirant lotion suitable for use with a roll-on or pump spray applicator.

	%
Treated powder	12.50
Ethanol	30.00
Glycine	5.00
Tween 20 (polyoxyethylene sorbitan monolaurate)	2.50
Water	50.00

Example 24.

The following is an example of a formula for a composition in the form of a stick for use with a stick applicator.

	%
Treated powder	20.00
Volatile silicone 7158' (Union Carbide)	48.00
Span 85 (sorbitan trioleate)	2.00
Ceto-stearyl alcohol	30.00

' Decamethylcyclopentasiloxane

The word "Span" is a trade mark.

Example 25.

The following is an example of an antiperspirant cream composition.

	%
Treated solution	85.70
Glyceryl monostearate (Arlacel 165)	10.00
Water	4.30

WHAT WE CLAIM IS:—

1. Method of inhibiting perspiration comprising applying to the skin a polymeric antiperspirant compound which is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound forms in water an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

2. A method as claimed in claim 1, wherein within said species there is contained from 5 to 60% by weight of the total aluminium.

3. A method as claimed in claim 1 or claim 2, wherein said basic aluminium compound has the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.4 to 1.5
the formula in the case of the compound in solid form containing 0.5 to 8 molecules of water of hydration.

4. A method as claimed in any of claims 1 to 3, wherein the basic aluminium compound has an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 4 to 1.6:1.

5. A package consisting of the combination of an antiperspirant composition comprising an antiperspirant active compound and an applicator for applying the antiperspirant composition to the skin, wherein the antiperspirant active compound is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound forms in water an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

6. A package as claimed in claim 5, wherein the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises a suspension of said antiperspirant active compound in particulate form in a liquid carrier.

7. A package as claimed in claim 6, wherein the antiperspirant active compound is suspended in a liquid vehicle comprising a mixture of a liquid carrier and a propellant.

8. A package as claimed in claim 5, wherein the applicator is a container fitted with a valve for dispensing liquid in aerosol form and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of said antiperspirant active compound.

9. A package as claimed in claim 8, wherein the composition also includes a propellant.

10. A package as claimed in claim 5, wherein the applicator is a roll-on applicator and the antiperspirant composition comprises an aqueous or aqueous alcoholic solution of the said antiperspirant active compound.

11. A package as claimed in claim 5, wherein the applicator is an applicator for dispensing a powdered material and the antiperspirant composition is a powdered composition including said antiperspirant active compound in powder form.

12. A package as claimed in any of claims 5 to 11, wherein within said species there is contained from 5 to 60% by weight of the total aluminium.

13. A package as claimed in any of claims 5 to 12, wherein said basic aluminium compound has the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.4 to 1.5
the formula in the case of the compound in solid form containing 0.5 to 8 molecules of water of hydration.

14. A package as claimed in any of claims 5 to 13, wherein the basic aluminium compound has an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 4 to 1.6:1.

15. An antiperspirant composition comprising an aqueous solution of an antiperspirant active compound in combination with an adjunct which is a perfume, thickener, alcohol or propellant, wherein said compound is a basic

aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, said aqueous solution containing polymeric species having a size greater than 100 Angstroms within which species there is present from 2 to 80% by weight of the total aluminium.

16. An antiperspirant composition as claimed in claim 15 in the form of a lotion comprising an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight and 0.1 to 5% by weight of a thickening agent.

17. An antiperspirant composition as claimed in claim 15 comprising an aqueous or aqueous alcoholic solution of the basic aluminium compound in a concentration of from 1 to 30% by weight and from 0.1 to 1% by weight of perfume.

18. An antiperspirant composition as claimed in claim 15 comprising an aqueous alcoholic solution of the basic aluminium compound containing from 1 to 60% by weight of an alcohol.

19. An antiperspirant composition as claimed in claim 15 comprising from 1 to 80% by weight of a propellant.

20. An antiperspirant composition comprising in combination a powdered antiperspirant active compound and a powdered inert solid diluent or organic liquid carrier, wherein said compound is a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound when dissolved in water forms an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

21. An antiperspirant composition as claimed in claim 20 in the form of a powder aerosol composition comprising a suspension of the basic aluminium compound in particulate form in a liquid carrier, said composition also comprising a propellant.

22. An antiperspirant composition as claimed in claim 21 in the form of a powder aerosol composition comprising

A. from 1% to 12% by weight of said basic aluminium compound in powder form;
B. from 0.1% to 5% by weight of a suspending agent;
C. From 1% to 15% by weight of a carrier liquid; and
D. from 70% to 96% by weight of a propellant.

23. An antiperspirant composition as claimed in claim 20 comprising from 5 to 40% by weight of said basic aluminium compound in powder form, the remainder consisting essentially of an inert powder material.

24. A composition as claimed in any of claims 15 to 23, wherein within said species there is contained from 5 to 60% by weight of the total aluminium.

25. A composition as claimed in any of claims 15 to 24, wherein said basic aluminium compound has the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.4 to 1.5
the formula in the case of the compound in solid form containing 0.5 to 8 molecules of water of hydration.

26. A composition as claimed in any of claims 15 to 25, wherein the basic aluminium compound has an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 4 to 1.6:1.

27. A solid antiperspirant compound comprising a hydrated basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, and which compound when dissolved in water forms an aqueous solution containing species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

28. A solid antiperspirant compound as claimed in claim 27 having the empirical formula

$$Al_2(OH)_{6-a}X_a\,nH_2O$$

where X is Cl, Br, I or NO_3
a is from 0.3/to 1.5
n is from 0.5 to 8.

29. A compound as claimed in claim 28, wherein a is from 0.5 to 1.5.

30. A compound as claimed in claim 28, wherein a is from 0.8 to 1.25.

31. A compound as claimed in any of claims 28 to 30, wherein n is from 0.5 to 4.

32. A solid compound as claimed in any of claims 27 to 31 in the form of particles having a size less than 100 microns.

33. An aqueous solution of an antiperspirant compound in a concentration of from 7 to 15% by weight, said compound being a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.3/to 1.5
said solution containing polymeric species having a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium present in said compound, said solution being free of boehmite as determined by X-ray diffraction on the material dried at 50°C under vacuum.

34. An aqueous solution of an antiperspirant compound, wherein said compound is a polymeric compound of empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.3/to 0.9
said solution containing polymeric species having a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

35. An aqueous solution of an antiperspirant compound, wherein said compound is a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 1.1 to 1.5
said solution containing polymeric species having a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

36. An aqueous solution of a basic aluminium bromide, iodide or nitrate having an aluminium to bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, which solution contains polymeric species of the basic aluminium compound of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

37. An aqueous solution of an antiperspirant compound in a concentration of from 1 to 60% by weight, said compound being a polymeric compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Br, I or NO_3
a is from 0.3/to 1.5
said solution containing polymeric species having a size greater than 100 Angstroms within which species is present from 2 to 80% by weight of the total aluminium.

38. An aqueous solution as claimed in claim 33 to 37, wherein a is from 0.4 to 1.25.

39. A compound or solution as claimed in any of claims 27 to 38, wherein within said species there is contained from 5 to 60% by weight of the total aluminium.

40. Process for making an aqueous solution of an antiperspirant compound comprising heating an aqueous solution of a compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Cl, Br, I or NO_3
a is from 0.3/to 1.5
said solution having a concentration of from 7 to 35% by weight, at a temperature of from 80°C to 140°C for a time sufficient to give rise in said solution to polymeric species having a size above 100 Angstroms in such amount that from 2 to 80% by weight of the total aluminium is contained within such species.

41. Process for making an aqueous solution of an antiperspirant compound comprising heating an aqueous solution of a compound of the empirical formula

$$Al_2(OH)_{6-a}X_a$$

where X is Br, I or NO_3
a is from 0.3/to 1.5
the concentration of such solution and its temperature and time of heating being such that there is produced in the solution polymeric species having a size above 100 Angstroms in such amount that from 2 to 80% by weight of the total aluminium is contained within such species.

42. Process for making an improved solid hydrated antiperspirant active compound comprising spray drying an aqueous solution of a basic aluminium chloride, bromide, iodide or nitrate having an aluminium to chloride, bromide, iodide or nitrate molar ratio of from 6.5 to 1.3:1, said solution containing polymeric species of a size greater than 100 Angstroms within which species there is contained from 2 to 80% by weight of the total aluminium.

43. Process as claimed in any of claims 40 to 42, wherein within said species there is contained from 5 to 60% by weight of the total aluminium.

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